Development of an Improved VOC Analysis Method for Architectural Coatings

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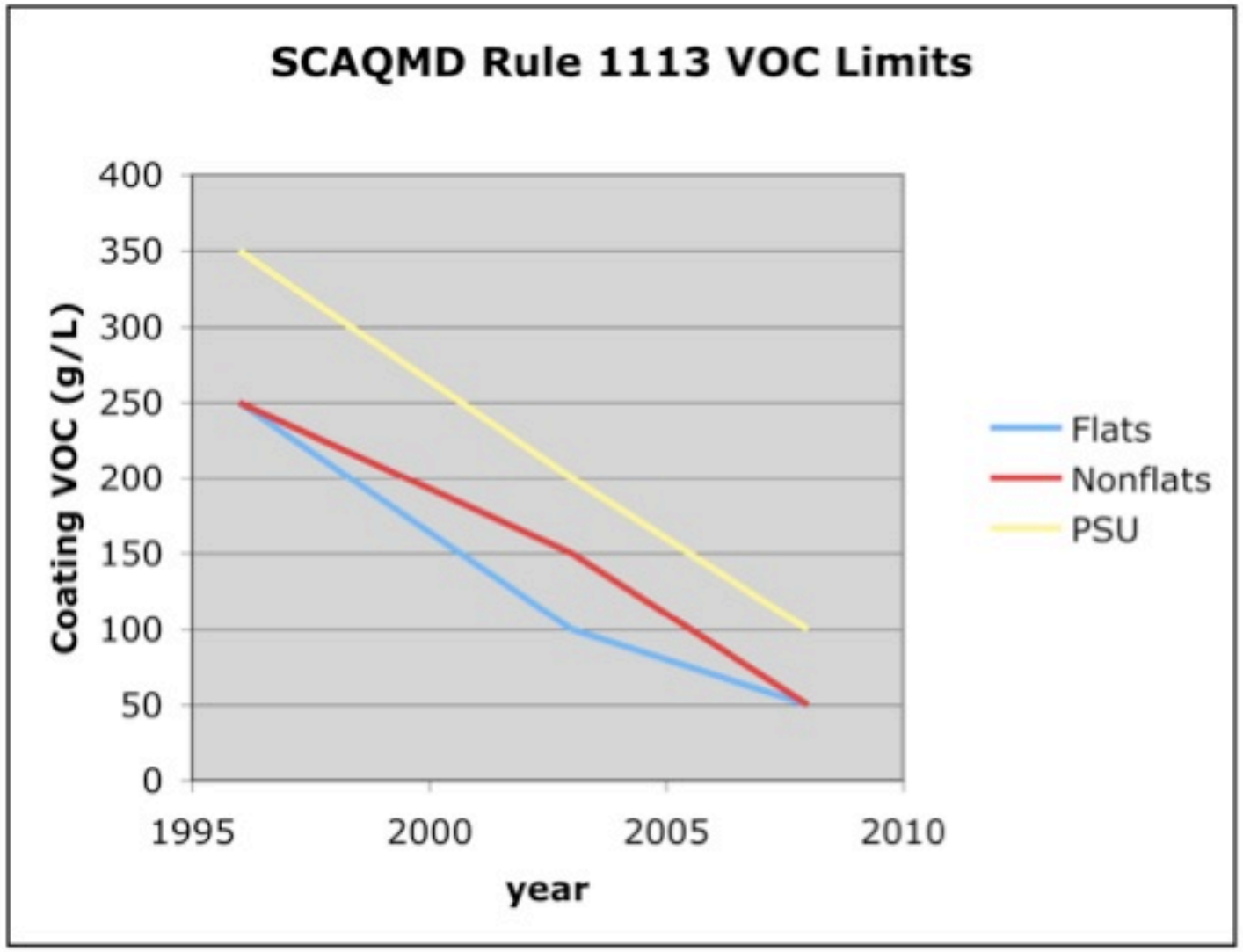
Overview

- Background: why new methods are needed: Indirect (EPA Method 24) vs. Direct (ASTM D6886) analysis
- Comparison of existing methods
- Coatings chosen for analysis
- New methods developed
- Results for samples studied
- Investigation of static headspace GC
- Results of validation studies (mini round-robin)
- Conclusions

VOC Definitions

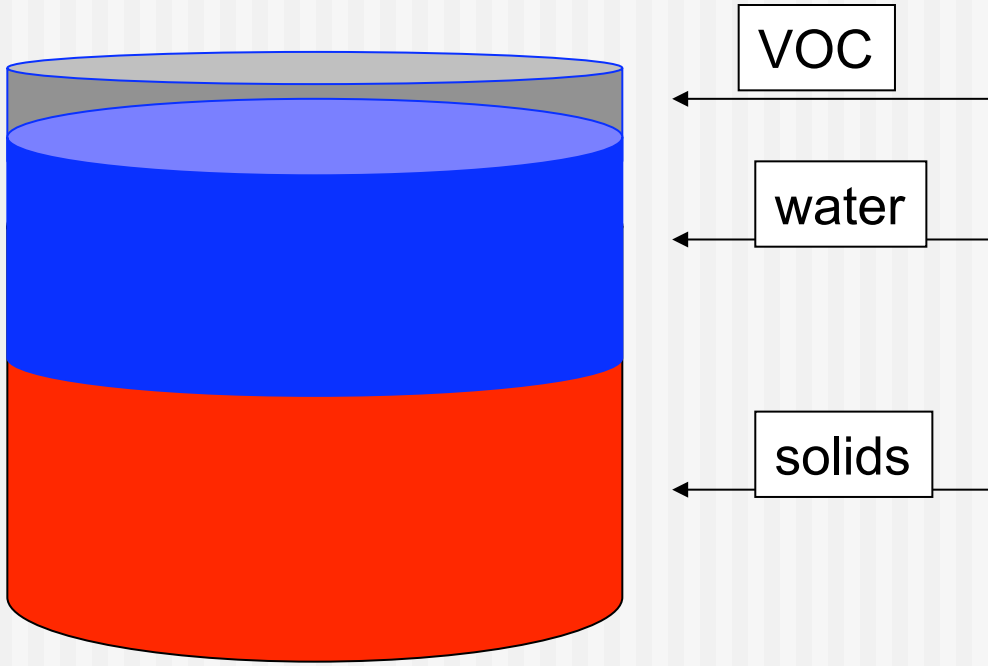
- VOLATILE ORGANIC COMPOUND (VOC) is any volatile compound of carbon, excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and exempt compounds which participates in atmospheric photochemical reactions.
- VOCs are “solvents” which “evaporate” from the coating during and after application, excluding exempt compounds
- **U.S.** VOCs are what you measure by EPA Method 24 (ASTM Practice D3960)
- **ISO (Europe)** VOCs are compounds with boiling points lower than diethyladipate (polar compounds) or tetradecane (non-polar compounds)

Why are we here?
Enforcement challenge



Traditional VOC Measurement

- Determine density of coating
  - Weight-per-gallon cup
- Determine “solids” of coating
  - Heat at 110°C for 1 hour
  - ASTM 2369
- Determine water in coating
  - GC or Karl-Fisher titration



VOC definitions

- Material VOC (regulatory VOC): grams of VOC per liter of coating

$$VOC_{material} = \frac{g_{VOC}}{L_{\text{paint}}}$$

- Coating VOC: grams of VOC per liter of coating – liters of water – liters of exempts

$$VOC_{coating} = \frac{g_{VOC}}{(L_{\text{paint}} - L_{\text{water}} - L_{\text{exempts}})}$$

Weight per gallon and solids

Weight per gallon cup

ASTM 2369:

paint + water or solvent, 110°C for one hour

Significance of ASTM 2369 solids determination

- Actually *defines* VOC
- Problems:
  - Depends on oven
  - Depends on paint matrix
    - Resin – type
    - Pigments
    - Additives
    - Multicomponent reactive coatings
  - Depends on amount of sample and water or solvent
    - ASTM currently examining for total revision – possibly no solvent
    - Different labs use different amounts of water/solvent

Water determination

- Karl Fisher titration
  - ASTM D4017
- Problems:
  - Size of sample
  - Matrix
  - Solvent
  - Uncertainty
- Gas Chromatography
  - ASTM D3892
  - Uncertainty

Experimental Data Used to Calculate VOC Values

f_V = **weight fraction of total volatile content (1 – weight fraction solids content)**

f_{VOC} = **weight fraction of VOC content**

f_W = **weight fraction of water content**

D_P = **density of paint in g/L**

D_W = **density of water in g/L**

f_{ex} = **weight fraction exempt solvent (must include term for each exempt solvent)**

D_{ex} = **density of exempt solvent in g/L**

VOC Calculations for Method 24 (no exempts)

Equations based on Method 24 (ASTM 3960) for coating and material VOC using indirect method:

$f_V - f_W = f_{VOC}$

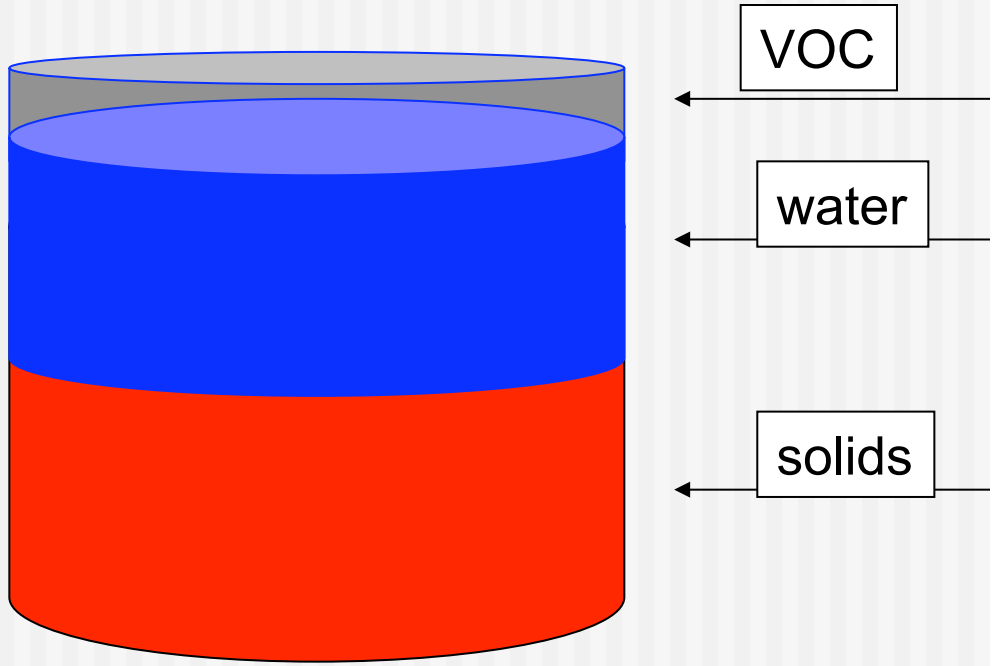
$$VOC_{coating} = \frac{(f_V - f_W)D_P}{1 - [f_W(D_P / D_W)]}$$

Large error for small f_{VOC}

$$VOC_{material} = (f_V - f_W)D_P$$

Direct VOC Measurement

- Determine density of coating
  - Weight-per-gallon cup
- Determine “solids” of coating
  - Heat at 110 C for 1 hour
  - ASTM 2369
- Determine fraction VOC *directly*
  - Gas chromatography
  - ASTM D 6886



Calculation of fraction VOC in sample

- Prepare sample with known amounts of possible analytes and internal standard(s)
- Obtain areas for each peak from GC
- Calculate relative response factors for each analyte
  - RF = AA x MI /(AI x MA) where AA and AI are areas of analyte and internal standard and MA and MI are masses of analyte and internal standard
- Prepare sample of coating with known mass of internal standard
- Obtain areas for each peak from GC
- Calculate fraction analyte for each analyte found
  - FA = (AA x MI)/(AI x RF)
- Total VOC fraction is sum of all analyte fractions

ASTM D 6886-03

Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatograpy

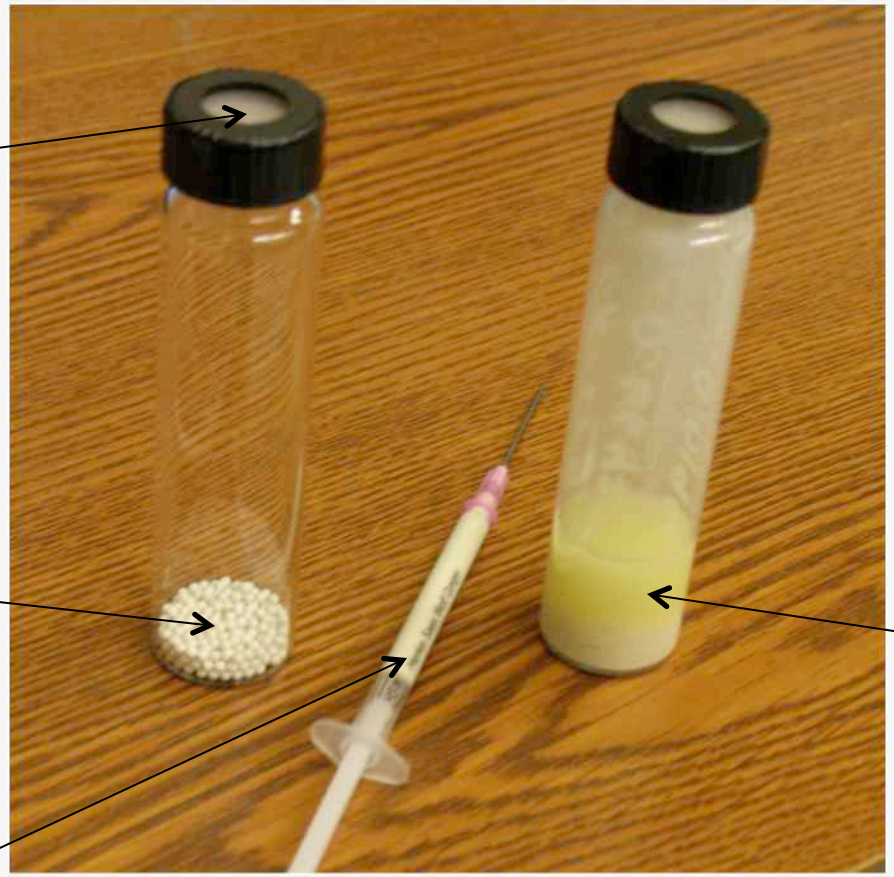
Assumptions

- For air-dry waterborne architectural coatings with a material VOC level below 5%, the number of different individual solvents will be a small, and
- The probable solvents are likely to be ethylene glycol(EG), propylene glycol(PG), ethylene glycol butyl ether(EB), diethylene glycol butyl ether(DB), and/or Texanol(TX).

Coating Analysis by Direct Injection (with modifications to ASTM D6886)

- Add 0.6 to 0.8 g of **coating** to a 20 or 40 mL vial containing 3-5 g of ceramic beads and 10mL of THF or acetone or IPA containing 1 mg/mL ethylene glycol diethyl ether (EGDE). Mix the contents by shaking.
- Alternatively, add 0.6-0.8 g of **coating** to a 20 or 40 mL vial containing ceramic beads and add 10.0mL of THF or acetone or IPA. Add 20 µL EGDE and reweigh. Mix the contents by shaking.
- Inject 1µL of the **coating** solution/dispersion into a GC with flame ionization detection and calculate the amount of each VOC present in the coating using experimental peak areas and measured response factors.

ASTM D6886 sample preparation



Gas chromatography columns

- Primary column: 30 m x 0.25 mm 5% phenyl/ 95% methyl siloxane (PMPS, DB-5), 1.0 μm film thickness (robust, common, relatively inexpensive)
- Confirmatory columns: 30 m x 0.25 mm polydimethylsiloxane (PDMS), 0.25 μm film thickness; 30 m x 0.25 mm Carbowax™ (CW), 0.25 μm film thickness.

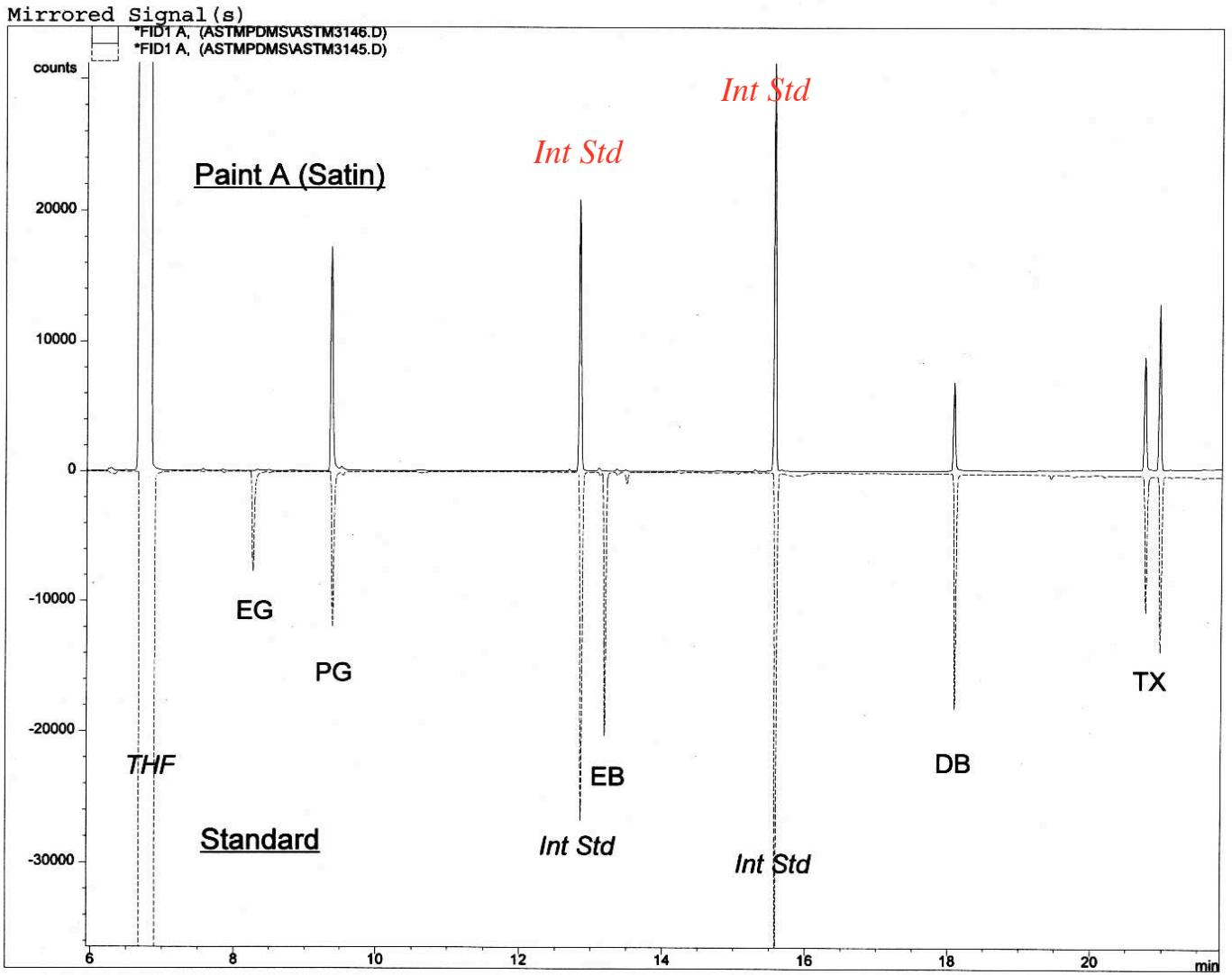
GC Parameters

- Carrier Gas: Helium

- Flow Rate: 1.0 mL per minute, constant flow (24.9 cm/sec at 40^{o}C)

- Split Ratio: Variable

- Temperatures, Inlet 260^{o}C, Detector 270^{o}C
  Initial temperature: 40^{o}C for 4 minutes
  Ramp: 10^{o}C/min to 250^{o}C, hold 5 min.


Mirrored Signal(s)
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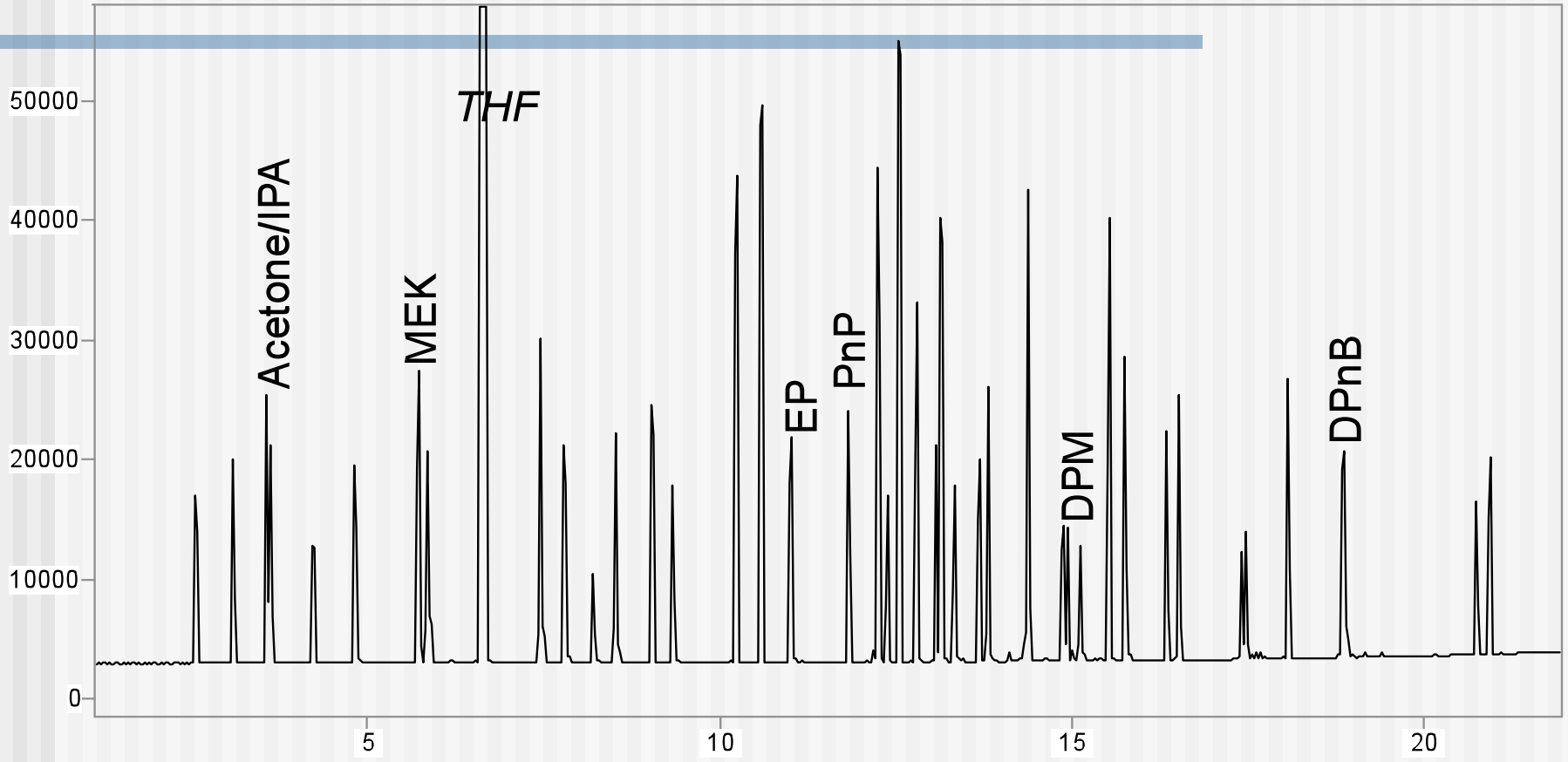
*FID1 A, (ASTMPDMS\ASTM3145.D)
counts
20000
10000
0
-10000
-20000
-30000
Paint A (Satin)
Int Std
Int Std
EG
PG
THF
EB
DB
TX
Standard
Int Std
Int Std
6
8
10
12
14
16
18
20
min

GC Retention Time Library



Counts / Minutes
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VOC methods used by California regulatory agencies

agency	method(s)	analysis	type of VOC analysis (indirect or direct)	uncertainties
California Air Resources Board (CARB)	310	VOCs and exempts in consumer products	indirect analysis of total volatile content, direct analysis of exempts using GC/FID	3% for total volatiles, none given for exempts
South Coast Air Quality Management District (SCAQMD)	313, 303	VOCs and exempts	direct analysis of VOC by GC/MS, exempt by GC/TC	none given
Bay Area Air Quality Management District (BAAQMD)	21, 22, 41, 43	VOCs and exempts in coatings	indirect analysis ot total volatile content, exempts by GC/TC and GC/FID	none given

Other VOC methods investigated

- The “Battelle” Method
  - mid 1990s, waterborne coatings, heat sample at 110^{o}C for one hour, collect volatiles on solid sorbent, desorb to GC
- EPC/ASC Method
  - Emulsion Polymers Council and Adhesive and Sealant Council
  - Static headspace, 25 mg sample, 10 min@ 150^{o}C, split and transferred to GC
  - Separate response factors for each sample, both GC-MS and FID
- EPA Method 311
  - HAPs by direct GC analysis
- ASTM D6133-02, ASTM D6439-99, ASTM D4457-02
  - Exempts by Direct GC (D6133 and D4457) and SPME-GC (D6439)

67 Coatings chosen for analysis

- Based on 2001 and 2005 CARB Architectural Coatings Surveys – covering all types sold in California
- No flats, nonflats, primer/sealer/undercoaters
  - Extensively studied previously by both indirect methods (based on EPA Method 24) and direct methods (based on ASTM D6886)
  - ASTM D6886 was developed specifically to deal with problems in determining VOCs of these coatings using EPA Method 24
- 11 two component (2K) coatings
  - 8 solventborne
  - 3 waterborne
- 8 coatings containing high levels of exempt solvents

		WATERBORNE					SOLVENTBORNE		
sample #	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
1	Fire Resistive	X							
2	Recycled	X							
3	Industrial Maintenance					X-2K			
4	Bituminous Roof	X							
6	Driveway Sealer	X							
7	Metallic Pigmented	X							
8	Faux Finishing		X						
9	Stains - Clear/Semitransparent				X				
10	Stains - Opaque	X							
14	High Temperature								X
14-1	Industrial Maintenance							X-2K	
14-2	Industrial Maintenance							X-2K	
14-3	Industrial Maintenance							X-2K	
15-1	Industrial Maintenance							X-2K	
15-2	Industrial Maintenance							X-2K	
15-3	Industrial Maintenance							X-2K	
24	High Temperature								X
25	Swimming Pool					X-2K			
26	Swimming Pool			X-2K					
29	Varnishes-clear		X						
32-1	Lacquers	X							
32-2	Primer/stainblock	X							
34	Dry Fog	X							
35	Dry Fog	X							
37	Roof	X							
38	Waterproofing Concrete/Masonry Sealers	X							
39	Bituminous Roof	X							
40	Driveway Sealer	X							
41	Driveway Sealer	X							
43	Roof	X							
44	Magnesite Cement								X
44-2	Magnesite Cement								X
45	Varnishes - Clear			X-2K					
48	Wood Preservatives				X				
50	Mastic Texture	X							
51	Waterproofing Concrete/Masonry Sealers	X							

		WATERBORNE				SOLVENTBORNE			
	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
52	Bond Breakers				X				
55	Rust Preventative		X						
56	Low Solids	X			X				
57-1	Lacquers						X		X
57-2	Lacquers						X		X
57-3	Lacquers						X		X
58	Concrete Stain				X				
60	Metallic Pigmented		X						
61	Varnishes - Clear		X						
62	Stains - Clear/Semitransparent								X
63	Floor		X						
64	Waterproofing Sealers				X				
65	Waterproofing Sealers	X			X				
73	Traffic Marking	X							
75	Bituminous Roof	X							
76-1	Faux Finishing		X		X				
76-3	Faux Finishing		X		X				
76-5	Faux Finishing		X		X				
77	Lacquer								X
79	Sanding Sealers				X				
80	Stains - Opaque	X			X				
81-1	Concrete Curing Compounds	X			X				
81-2	Concrete Curing Compounds	X			X				
82-1	Waterproofing Concrete/Masonry Sealers	X			X				
82-2	Waterproofing Concrete/Masonry Sealers	X			X				
83	Quick Dry Primer, Sealer, and Undercoater	X							
84	Shellacs - Clear						X		
85	Shellacs - Clear						X		
86	Wood Preservatives	X			X				
87	Varnish						X		

1. "Low VOC": <=3% VOCs by weight. "High VOC": >=10% VOCs by weight. "High Exempt": >=10% Exempt Compounds by weight.
2. "High Multi": Categories that have more than 10% multi-component products, by sales volume.
3. "Low Solids": 0-20% solids by volume. "High Solids": 80-100% solids by volume.
4. "Low Solids" and "High Solids" products only include single-component coatings.
   The other classifications include both single-component and multi-component coatings.

Summary of new methods developed as part of this project

- Standard Test Method for Direct Analysis of the Volatile Organic Compounds (VOCs) in Waterborne Air-Dry Coatings by Gas Chromatography (Waterborne Method). This method is a revision of ASTM Method D6886, Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography.
- Standard Test Method for Direct Analysis of the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography (2K Method)
- Standard Test Method for the Direct Analysis of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography (HAP Method)
- Standard Test Method for Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D2369 (Film Extraction Method)
- Standard Test Method for Solids Determination of 2K Coatings Containing More than 90% Solids (High Solids Method)

Standard Test Method for Direct Analysis of the VOCs in Waterborne Air-Dry Coatings by GC

- **Revision of ASTM Method D6886**
  - **Initially for waterborne coatings with < 5% VOC**
- **Expand for use with solventborne coatings**
- **Use to determine exempt VOC content (acetone, methyl acetate, p-chlorobenzotrifluoride, t-butyl acetate) of waterborne and solventborne coatings**
- **Expand possible solvents to include THF, acetone and 2-propanol**
- **Use ethylene glycol diethyl ether (EGDE) as internal standard**
- **Use small, inert ceramic beads to insure complete mixing**

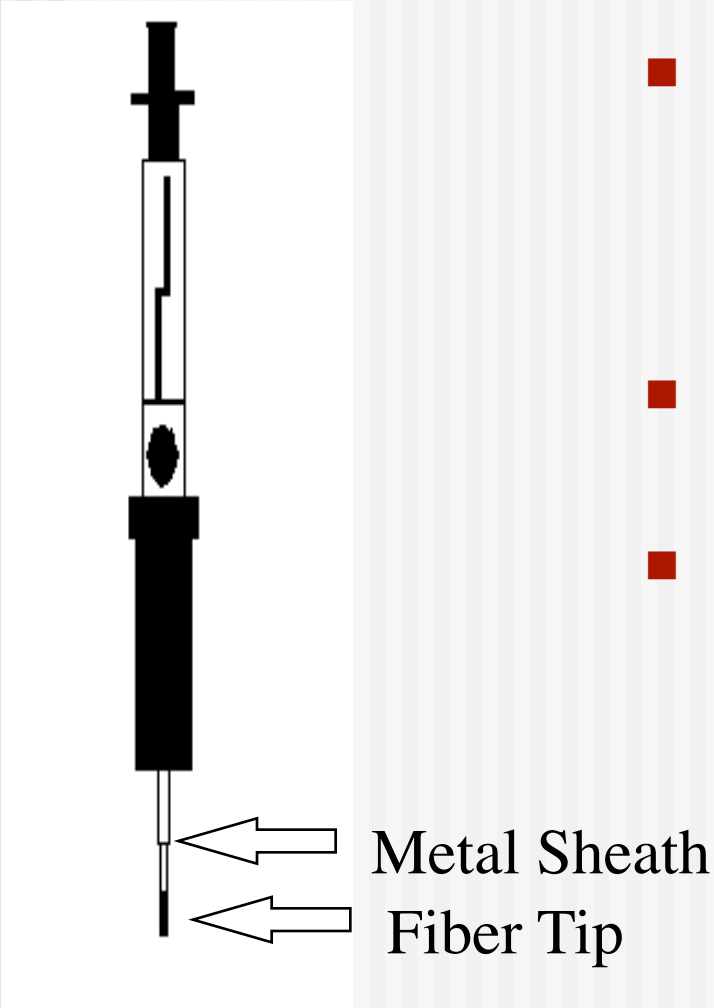
Standard Test Method for the VOC and HAP Content of Multi-Component Coatings by GC

- Use for solventborne and waterborne multi-component coatings curing by chemical reaction and coatings which cure by heating (i.e. melamine-cure coatings and powder coatings)
- Prepare 100 grams of mixed coating, transfer 100 mg to 20mL headspace vial, seal and allow to cure for 24-26 hours at ambient temperature
- Heat sample for 30 minutes at 110^{o}C, cool, add known quantity of acetone containing internal standard, and mix.
- Solution analyzed by gas chromatography using 5% phenyl/95% polydimethylsiloxane (PMPS) capillary column
- May use THF as solvent if sample contains acetone.
- Acetone and isopropyl alcohol may coelute. If either present, confirm using Carbowax^{TM} capillary column. Other possible coeluting compounds are PM acetate/ethylbenzene, 2-butoxyethanol/o-xylene – can adjust heating rate using PDMS column
- **Sample cures under application conditions with no added solvent**
- **Obtain total fraction VOC and fractions of any exempt solvents and HAPs**

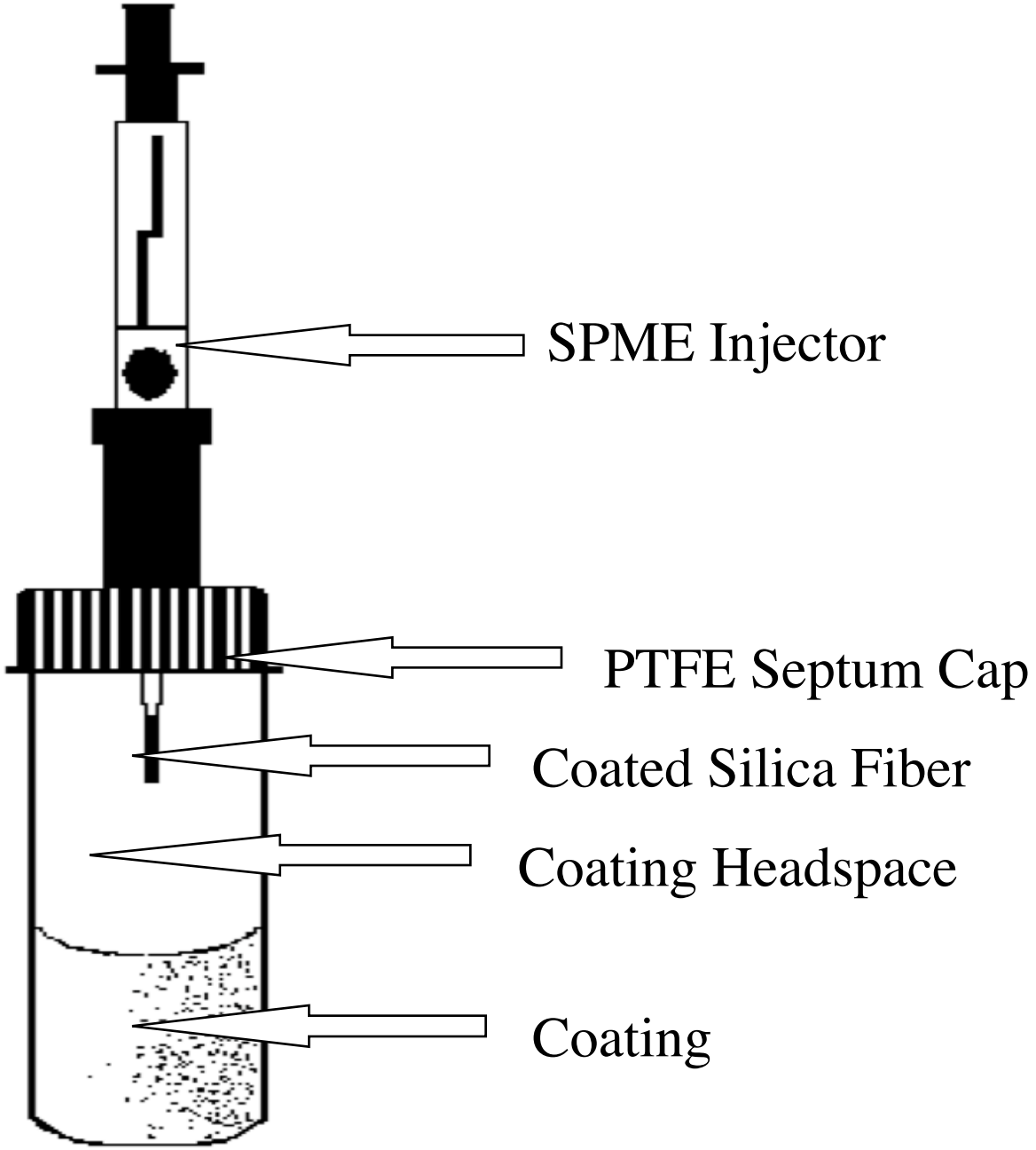
Standard Test Method for Determination of Common HAPs in Solventborne Air-Dry Coatings by GC

- Determine MIBK, toluene, commercial xylene, cumene, naphthalene if present at 0.01 weight percent or greater
- Known weight of coating dispersed in THF or acetone, internally standardized, analyzed by GC to give speciated composition of VOCs including HAPS
- Solid phase microextraction (SPME) using GC/FID or GC/MS may be used for identification of VOCs present
- Possible co-eluting compounds can be separated using PMPS column by varying heating rate
- Cumene introduced from Aromatic 100
- Naphthalene introduced from Aromatic 150

Solid Phase Microextraction (SPME) in Coatings Analysis



- Fused-silica fiber tip coated with Carbowax-divinylbenzene (or other adsorbing material) is placed in contact with coating headspace
- Solvent molecules in headspace are adsorbed and concentrated on fiber
- Fiber is withdrawn into protective metal sheath and inserted into hot GC injection port where solvent molecules are thermally desorbed onto column


SPME Injector
PTFE Septum Cap
Coated Silica Fiber
Coating Headspace
Coating

Standard Test Method for Determination of the Semi-volatile Content Remaining in Paint Films after ASTM Method D2369

- Fundamental difference between EPA Method 24 and ASTM D6886
  - For EPA Method 24, semi-volatiles remaining in the paint film after ASTM D2369 are not counted as VOCs
  - For ASTM D6886 (direct analysis) the total amount of all semi-volatiles in the paint is determined
  - For consistency, the amount of semi-volatiles remaining in the film must be subtracted from the amount obtained using the direct method
- Immediately after a D2369 determination (solids), the aluminum pans are cut up, placed in a 125 mL Erlenmeyer flask, and 20 mL of acetone or MEK are added. Flask is stirred for 12-24 hours, extracting remaining VOCs from film
- 5.0 mL of THF or acetone with internal standard added, and solution analyzed using GC
- VOCs with BP > 250^{o}C and retention times ≥ Texanol® are determined.
- Peaks may appear in chromatogram not seen in original unheated sample due to oxidative degradation
- VOCs obtained from the extracted sample are subtracted from the original VOC amount obtained from the unheated sample

Standard Test Method for Solids Determination of 2K Coatings Containing More than 90% Solids

- US EPA approved revision of Sect. 7 of ASTM D2369 for coatings with > 90% solids
  - Concern over film thicknesses for these coatings – not representative of application conditions
  - Concern over effect of solvent on rate of cure
- Use specimen weight consistent with lowest thickness manufacturer's literature recommends:

Weight(g) = thickness(mm) x 3.14 X [dish diameter^2 (mm^2)/4] x density (g/cm^3)/1000

- Use **no solvent** – spread sample with paper clip

Recommended VOC Analysis Methods

Coatings Type	Recommended Methods
Air-dry waterborne coatings without exempt solvents, VOC content < 10%	Revised D6886 and Extraction Method
Air-dry waterborne coatings without exempt solvents, VOC content >10%	Revised D6886 or EPA Method 24
Air-dry solventborne coatings, without exempt solvents	EPA Method 24; Use Revised D6886 and HAP Method if HAP content is to be measured
Air-dry solventborne coatings, with exempt solvents	Revised D6886 to determine exempt solvents and speciated VOC content
Solventborne 2K coatings, solids content < 90%	EPA Method 24 for mass-based VOC content; new 2K method if HAP content or speciated content is desired
Solventborne 2K coatings, solids content >90%	EPA Method 24 with new High Solids volatile method
Waterborne 2K coatings	New 2K method
Coatings containing Silanes, Siloxanes and Silane-Siloxane Blends	ASTM D5095 for total volatile content and new D6886 for speciation
Coatings containing semi-volatile organic compounds and/or with boiling points greater than 250°C and D 6886 primary capillary column retention time greater than Texanol®	Revised D6886 and Extraction Method

Precision values used in EPA Method 24

	ASTM Method	Repeatability r	Reproducibility R
Density	D1475-03	0.6%	1.8%
Volatile Content	D2369-04	1.5%	4.7%
Water by Karl-Fischer (KF) titration	D4017-02	3.5%	5.5%
Water by KF/methanol extraction	D4017-02	2.28%	7.46%
Water by KF/with homogenization	D4017-02	2.2%	4.2%
Water by GC	D3892-06	2.8%	5.0%

Precision values for exempt compounds

exempt solvent	ASTM method	Repeatability r	Reproducibility R
acetone	D6133-02	0.05	0.245
parachlorobenzotrifluoride	D6133-02	0.027	0.124
methyl acetate	D6133-02	0.046	0.293
t-butyl acetate	D6133-02	0.038	0.156
acetone	D6438-99	0.0118	0.0194
parachlorobenzotrifluoride	D6438-99	0.0097	0.0147
methyl acetate	D6438-99	0.0046	0.007
dichlormethane	D4457-02	0.03	0.179
1,1,1-trichloroethane	D4457-02	0.03	0.081

Precision values used in VOC determination based on ASTM D6886

	ASTM Method	Repeatability r	Reproducibility R
Density	D1475-03	0.6%	1.8%
Volatile Content	D2369-04	1.5%	4.7%
VOC fraction	D6886-03	7.5%	16.2%

Methods to estimate uncertainty in VOC measurements

Calculate maximum and minimum values based on precision in one variable

- Assumes most of total error results from error in one quantity, for example, f_w (for EPA Method 24) or f_{VOC} (for direct method based on ASTM D6886)

Calculate overall error using propagation of errors method

- For a function F(x,y,z)

$$\sigma_F = \left[\left(\frac{\partial F}{\partial x} \right)^2 \sigma_x^2 + \left(\frac{\partial F}{\partial y} \right)^2 \sigma_y^2 + \left(\frac{\partial F}{\partial z} \right)^2 \sigma_z^2 \right]^{0.5}$$

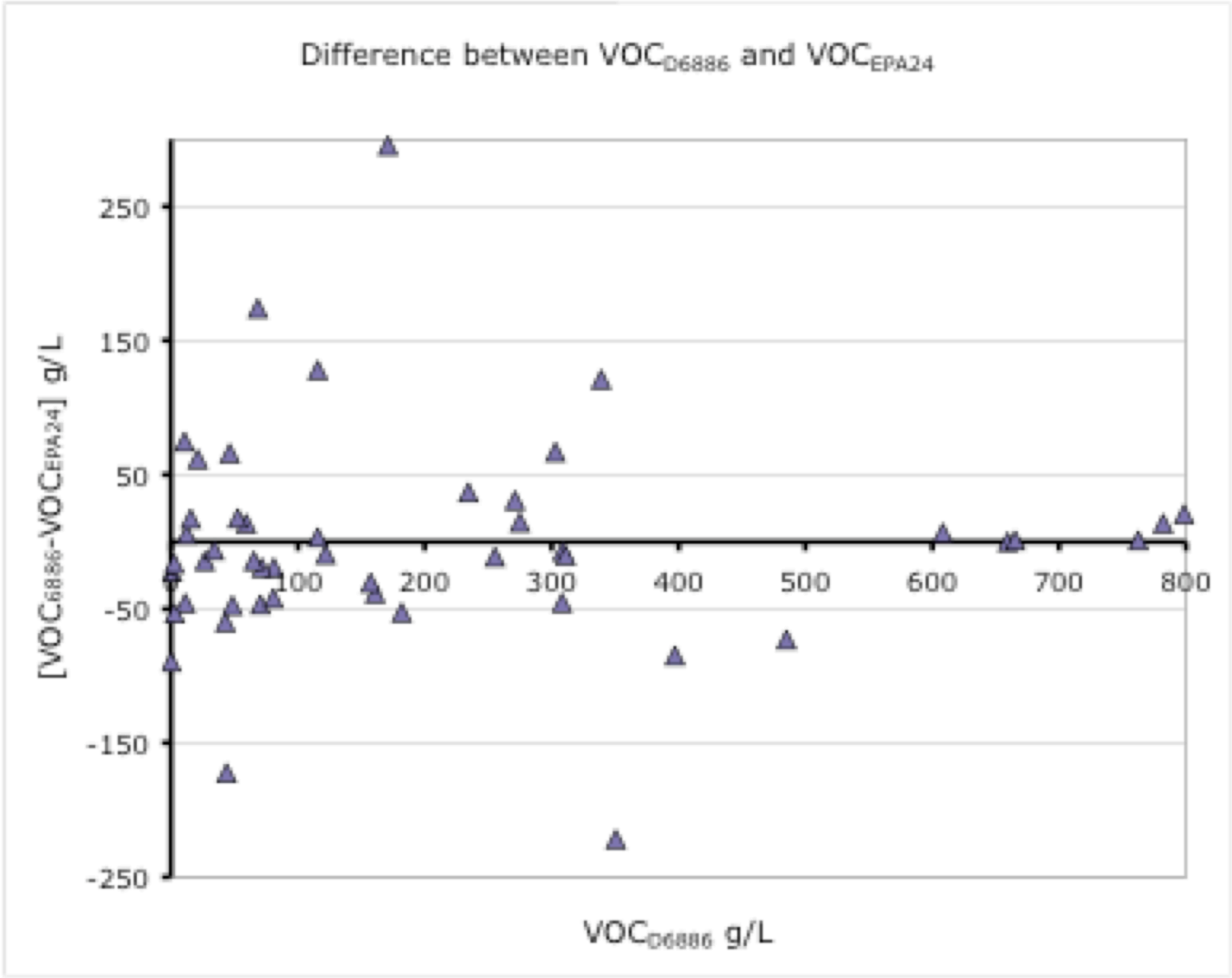
Water-borne Coatings from the 2001 ARB Coatings Survey

VOC results derived from 2001 ARB Coatings Survey						Uncertainties/(g/L)			
						Method 24		Direct Method	
coating class	fv	fw	fvoc	Dp	VOCreg (g/L)	inter-laboratory	intra-laboratory	inter-laboratory	intra-laboratory
Concrete Curing Compounds	0.78	0.74	0.040	1018.3	165	207	102	25	11
Fire Retardant - Clear	0.55	0.54	0.010	1186.02	33	127	66	5	2
Fire Retardant - Opaque	0.43	0.40	0.030	1365.72	90	86	43	14	6
Flat	0.47	0.44	0.030	1365.72	103	106	53	16	7
Industrial Maintenance	0.45	0.37	0.080	1329.78	209	70	32	28	13
Lacquers	0.68	0.56	0.120	1030.28	292	95	42	36	16
Nonflat - High Gloss	0.54	0.46	0.080	1209.98	218	88	41	29	13
Nonflat - Low Gloss	0.51	0.47	0.040	1281.86	129	106	52	19	9
Nonflat - Medium Gloss	0.56	0.50	0.060	1209.98	184	106	51	26	12
Recycled	0.51	0.42	0.090	1269.88	245	81	37	31	14
Roof	0.43	0.41	0.020	1269.88	53	78	40	8	4
Varnishes - Clear	0.69	0.58	0.110	1042.26	290	105	47	36	16
Wood Preservatives	0.86	0.82	0.040	1018.3	247	327	156	40	17

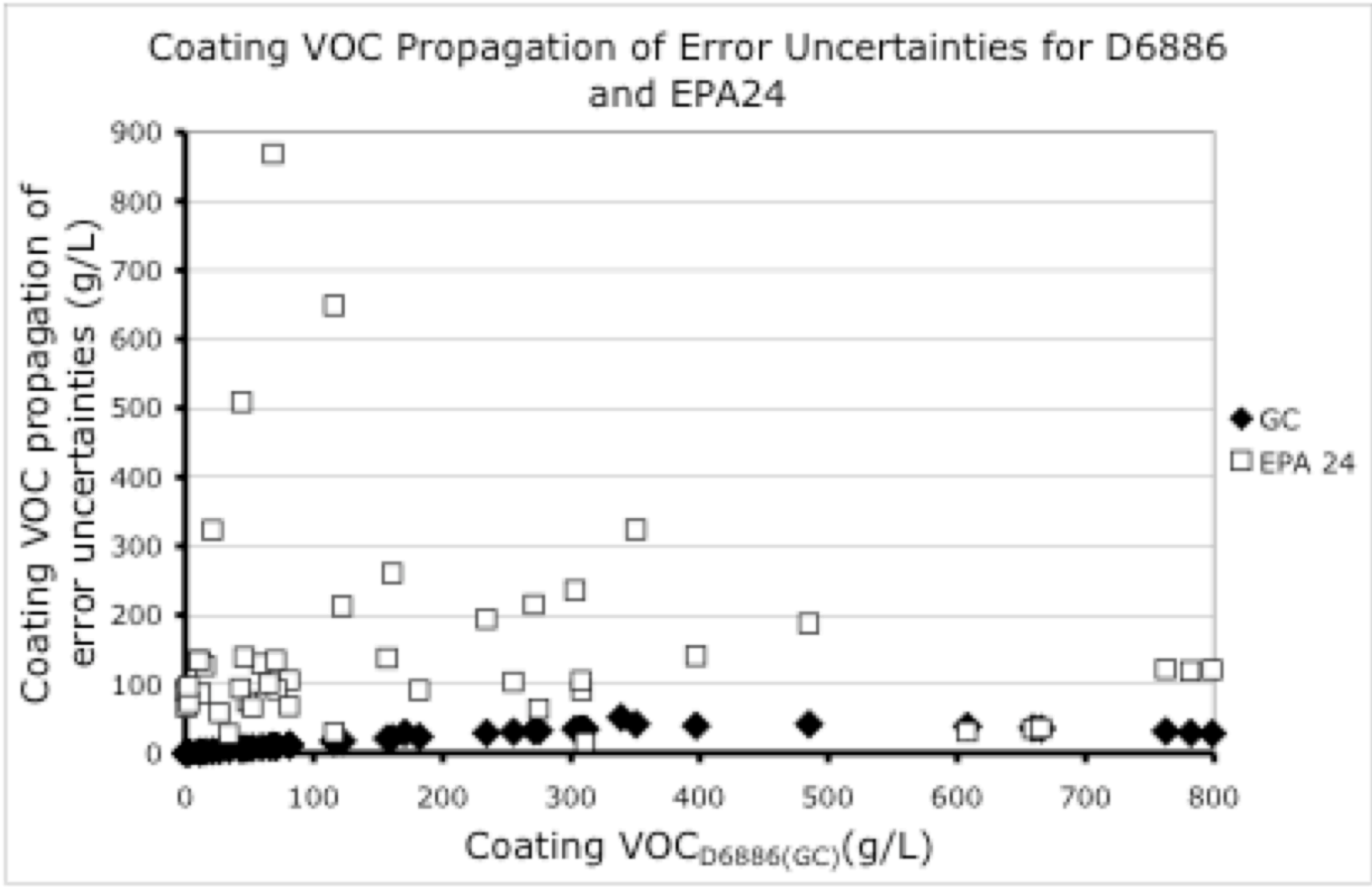
Sample results and uncertainties

				ASTM D6886				EPA Method 24			
					propagated error		VOC range		propagated error		VOC range
Coating Type	fv	fvoc	Dp (g/L)	VOC	based on R values	based on r values	VOCdirect R=16.2%	VOC	based on R values	based on r values	KF water R=4.2%
Fire Resistive	0.522	0.005	1047	12	2	1	4	6	86	45	100
Recycled	0.493	0.016	1342	59	9	4	18	45	130	67	147
Bituminous Roof	0.474	0.000	1035	1	0	0	0	23	66	34	76
Driveway Sealer	0.438	0.000	1372	0	0	0	0	89	91	46	99
Metallic Pigmented	0.637	0.021	1096	70	11	5	21	117	134	67	144
Faux Finishing	0.786	0.102	1063	397	40	20	78	482	141	56	94
Stain, Semitransp	0.823	0.031	1018	161	22	11	44	199	261	127	272

Differences between VOC_{D6886} and VOC_{EPA24} for samples analyzed



VOC uncertainties based on propagation of error calculations for ASTM 6886 and EPA 24



VOCs identified in 67 coatings samples

solvents identified		
(4-methylphenyl)phenylmethanone	butyl carbitol	naphthalene
1-butanol	cumene	N-methylpyrrolidinone
1-propanol	dibutyl phthalate	nonane
2-(2-ethylhexyl)ethanol	diethylene glycol monomethyl ether	o-xylene
2-butanol	diisopropyl naphthalene	parachlorobenzotrifluoride
2-butoxyethanol	dipropylene glycol monobutyl ether	phthalic anhydride
2-ethoxyethanol	dipropylene glycol monomethyl ether	polynuclear aromatic HCs
2-ethylhexanol	dipropylene glycol monopropyl ether	propylene glycol
2-ethylhexylbenzoate	ethanol	propylene glycol monobutyl ether
2-heptanone	ethylbenzene	propylene glycol monomethyl ether acetate
2-methylphenoxy oxirane	ethylene glycol	propylene glycol monophenyl ether
2-pentanone	furfuryl alcohol	propylene glycol monopropyl ether
2-propanol	glycerin	propylene glycol mono-t-butyl ether
2-propoxyethanol	m,p-xylene	p-xylene
4-methyl-3-heptanone	metachlorobenzotrifluoride	Stoddard Solvent
5-methyl-3-heptanone	methanol	styrene
acetaldehyde	methyl acetate	Surfynol
acetone	methyl ethyl ketone	tetrachloroisopthalonitrile
Aromatic 100	methyl isobutyl ketone	Texanol
benzophenone	methyl isopropyl ketone	toluene
benzyl alcohol	mineral spirits	triethyl amine
bis-2-ethylhexyl maleate	morpholine	triethylene glycol
butyl acetate		

Samples with exempt solvents

Sample #	#14	#24	#44	#44-2	#57-1	#57-2	#57-3	#77
coating category	industrial maintenance	high temperature	magnesite cement	megnesite cement	lacquers	lacquers	lacquers	lacquers
acetone fraction, avg		0.1816	0.248	0.4694	0.3824	0.5366	0.3674	0.2845
PCBTF fraction, avg	0.47							
methyl acetate fraction, avg					0.0042	0.0016	0.0418	
direct VOC fraction by GC, avg	0.1795	0.2961	0.2736	0.2417	0.3773	0.2908	0.3695	0.3266
indirect VOC fraction by EPA 24	0.1279	0.2513	0.2589	0.2066	0.352	0.2512	0.347	0.3877
	VOC values in g/L							
Material VOC, GC, avg	211	335	290	213	343	257	332	307
Coating VOC, GC, avg	355	452	434	448	617	645	611	464
Material VOC, EPA 24	150	284	274	182	320	222	312	365
Coating VOC, EPA 24	253	384	410	383	576	557	573	551
Material VOC, reported			269	192	269	232	294	343
Coating VOC, reported	312	<420	416	419	550	550	550	547
propagated error based on GC/ASTM 6133 R	31	41	39	36	49	44	49	41
propagated error based on GC/ASTM 6438 R	28	37	35	28	39	32	39	35

Results for 2K coatings

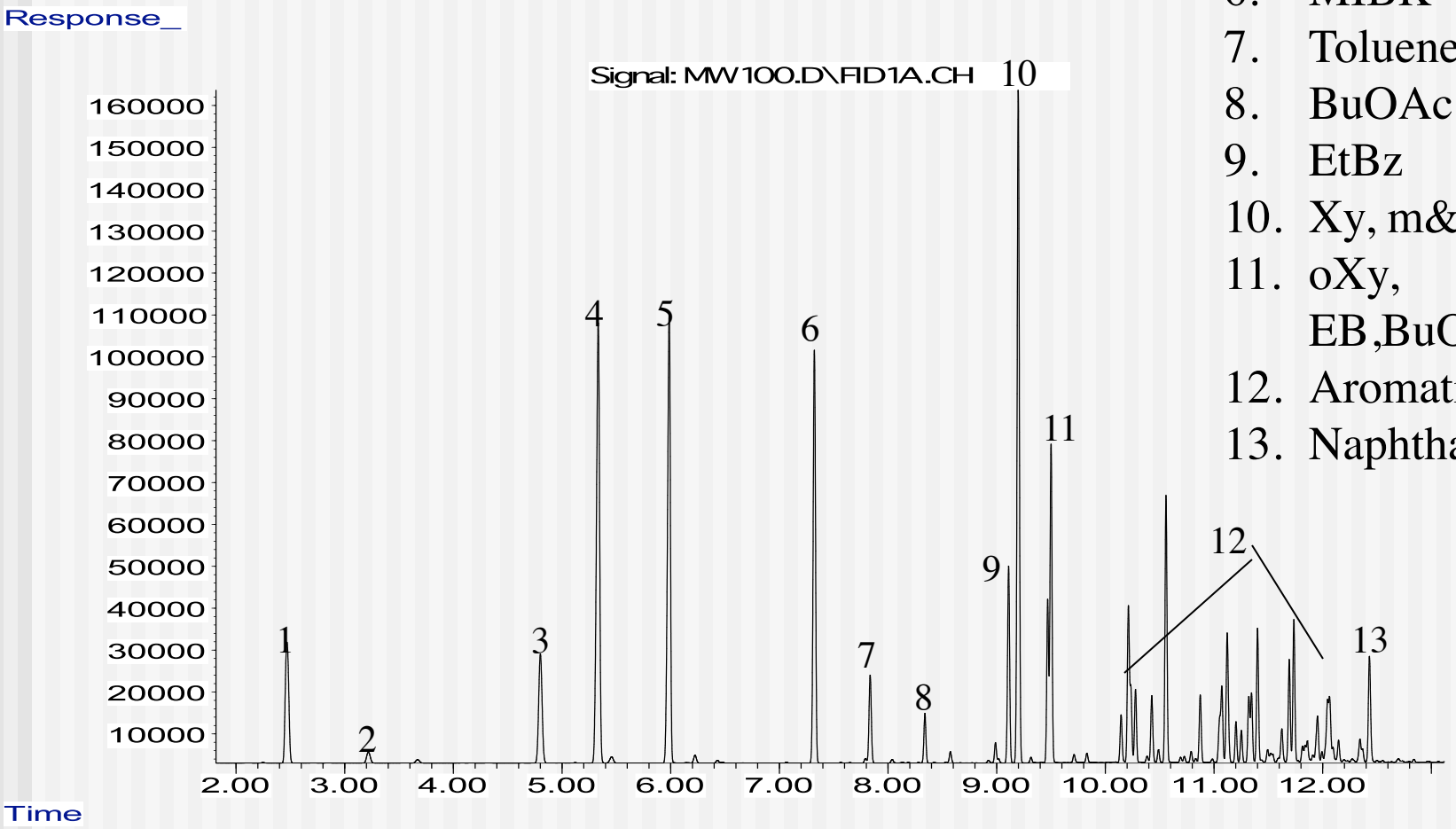
				Coating VOC g/L			Material VOC g/L	
Sample #	coatings category	solids fraction	water fraction	EPA24	GC/ave	reported	GC/ave	reported
#3	industrial maintenance	0.8803		168	178	179.7		
#14-1	industrial maintenance	0.9697		41	46	7		
#14-2	industrial maintenance	0.8557		241	261	296		
#14-3	industrial maintenance	0.8826		209	216	170		
#15-1	industrial maintenance	0.9739		34	19	10		
#15-2	industrial maintenance	0.9612		54	87	12		
#15-3	industrial maintenance	0.8448		225	211	214		
#25	swimming pool	0.8147		291	305	325		
#26-WB	swimming pool	0.5682	0.3191		226	236	138	122
#45-WB	varnishes clear	0.2824	0.6363		247	244	83	82
#59-WB	floor	0.6447	0.3147		90	<100	54	

Static headspace analysis: Agilent 6890N GC/5973 MS/G1888 static headspace analyzer

Sample Preparation

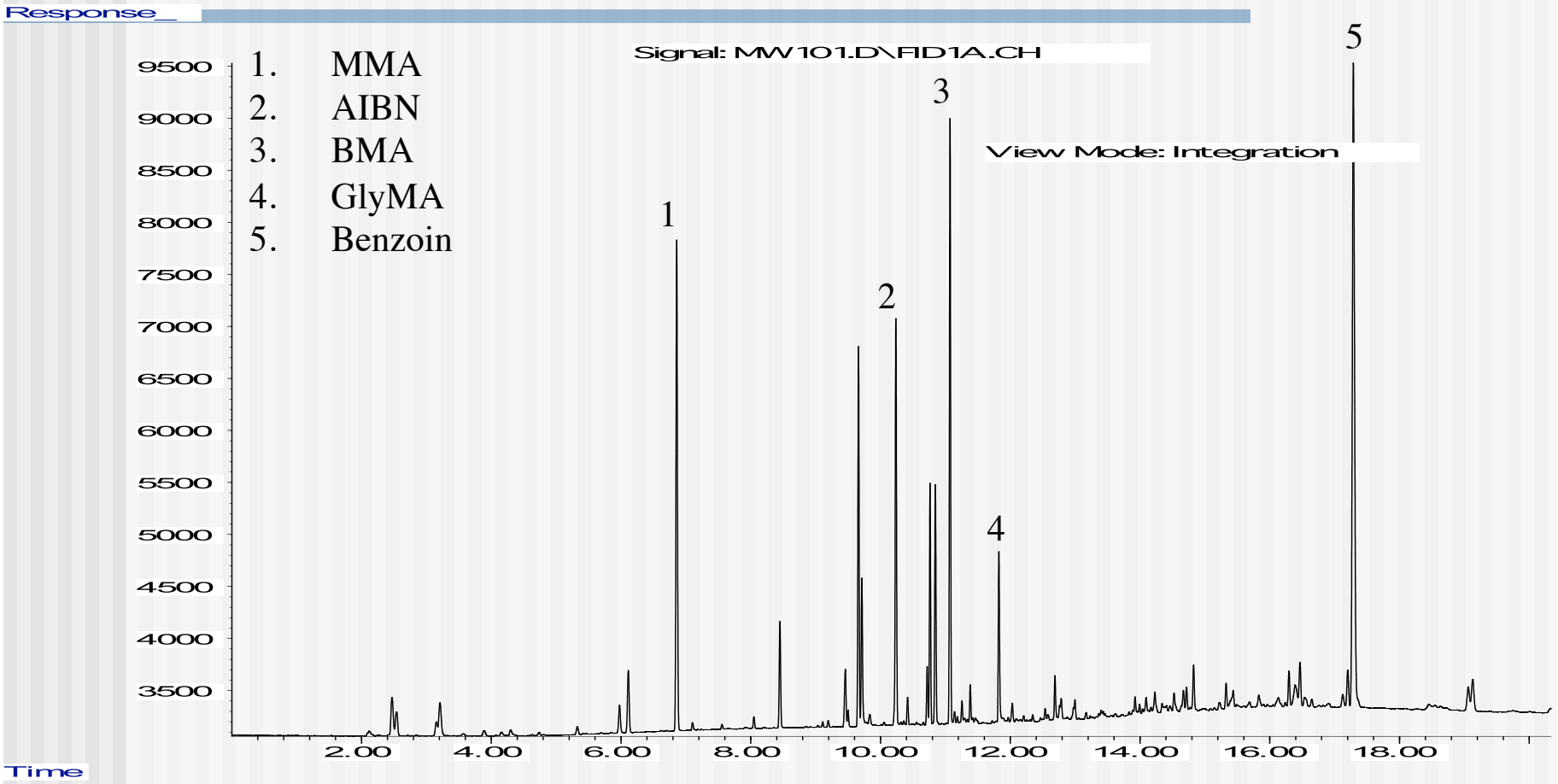
- Add neat coating to 20mL vial containing ceramic media
- Add internal standard and mix
- For waterborne, add 10.0mL internal standard in water and mix
- Transfer 10-20 mg of above to 20mL headspace vial
- Equilibrate for 20 minutes in headspace oven

Headspace GC of a SB melamine-cure automotive primer



1. Methanol
2. IPA
3. MEK
4. iBuOH
5. nBuOH
6. MIBK
7. Toluene
8. BuOAc
9. EtBz
10. Xy, m&p
11. oXy, EB,BuOPr
12. Aromatics
13. Naphthalene

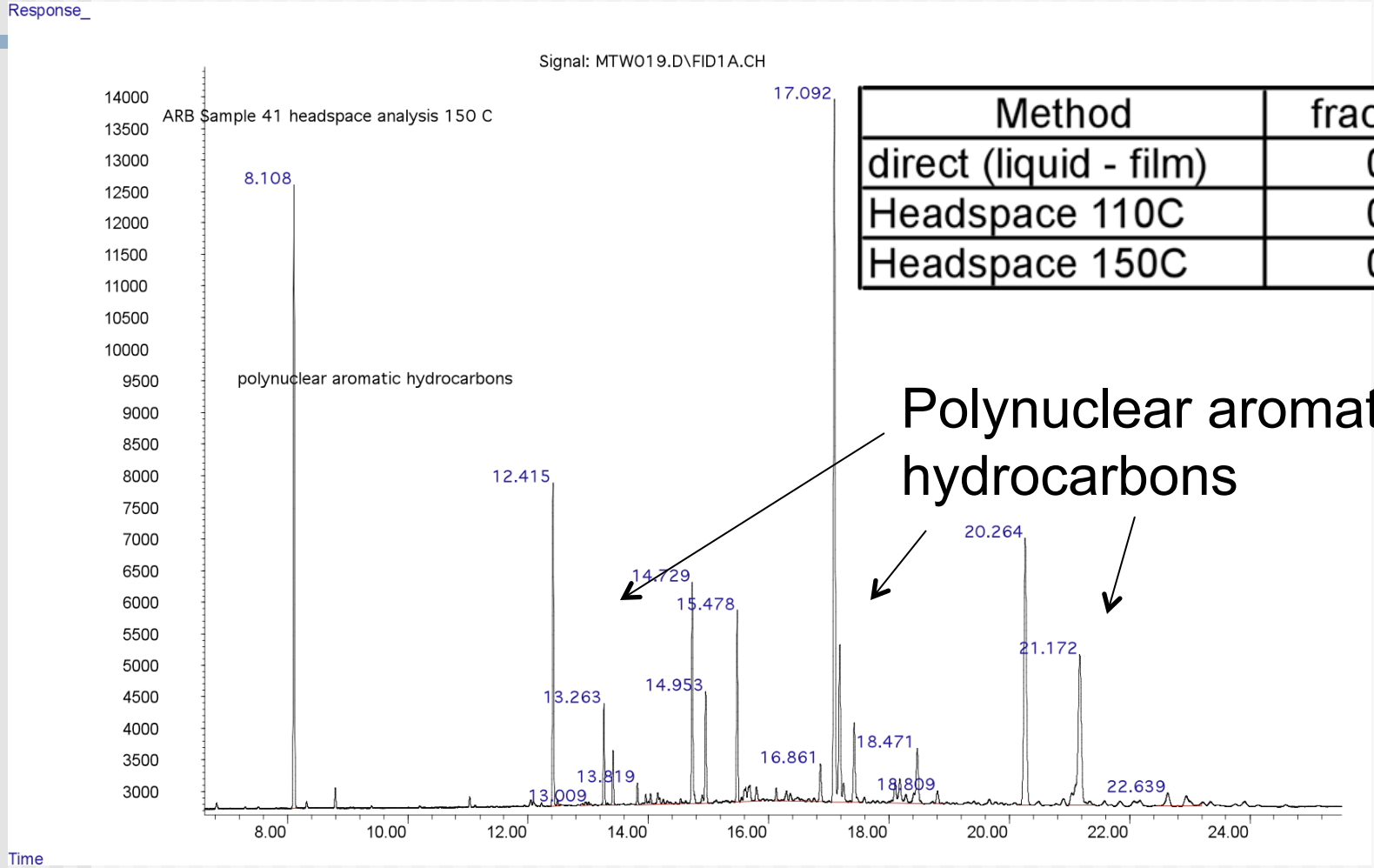
Headspace GC of a GMA Acrylic Powder Coating



Headspace GC of melamine-cure automotive primer

	Headspace, 150°C,rate 3°C/min	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
HCHO	0.025		
MeOH	4.02		
MEK	1.65	1.50	1.76
MIBK	3.47	3.42	3.51
Toluene	0.49	0.46	0.48
EtBz	1.21	1.10	0.99
m,p-Xy	3.49	3.51	
o-Xy	0.81	0.84	
xylenes	4.30	4.35	4.46
EB	1.47	1.68	1.81
Cumene	0.05	0.05	0.06
Napth	0.45	0.56	0.53

Headspace analysis of waterborne driveway sealer (#41)



Method	fraction VOC
direct (liquid - film)	0.0215
Headspace 110C	0.0191
Headspace 150C	0.0383

Polynuclear aromatic hydrocarbons

Comparison of headspace and direct analysis of semi-volatiles

Sample	coalescent	VOC fraction, direct injection, D6886	VOC fraction remaining in film after D2369	% VOC remaining in film after D2369	VOC fraction, static headspace, 110°C	VOC fraction, static headspace, 150°C
1	Texanol®	1.29	0.07	5.4	1.06	1.13
2	Semivol 1	1.07	0.60	56	0.38	1.14
3	Semivol 2	0.76	0.62	82	0.15	0.84

Static headspace analysis: conclusions

- Headspace analysis is useful for analysis of high-boiling volatiles – no need to analyze dried film
- Headspace analysis may be useful for analysis of semi-volatiles
- Headspace analysis allows sample to be tested under actual curing conditions – useful for powder coatings and high-temperature cure coatings
- Headspace cannot provide consistent analyses of highly polar analytes, such as glycols
- More work is needed before static headspace can be included in VOC analysis methods

Validation studies
mini round-robin

- Coatings in three categories sent to other laboratories
    - 2K coatings
    - unusual coatings (low solids, high VOC, unusual solvents
    - coatings with exempt solvent
- Samples split from coatings received from manufacturers
- Samples sent to five laboratories
    - two industrial laboratories (one did no analyses)
    - three regulatory agencies
        - CARB, BAAQMD, SCAQMD
- Provided information on our results and analysis procedures
    - Most labs used their own analysis methods

Samples selected for validation studies

Sample #		Category		Type	solids (lb/gal)
3		Industrial Maintenance		2K, high solids	10.31
VOCs	furfuryl alcohol	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
15-2		Industrial Maintenance		2K, high solids	11.11
VOCs	benzyl alcohol				
15-3		Industrial Maintenance		2K, high solids	10.24
VOCs	1-butanol	toluene	ethylbenzene	m,p-xylene	o-xylene
	cumene	Aromatic 100	benzyl alcohol		
26		Swimming Pool		2K	5.77
VOCs	2-propoxyethanol	Aromatic 100			
45		Varnishes - Clear		2K	2.46
VOCs	propylene glycol monomethyl ether	benzyl alcohol			
86		Wood Preservatives		low solids, high water	0.33
VOCs	ethylene glycol	propylene glycol monopropyl ether	1-iodo-2-propynyl butyl carbamate		
76-1		Faux Finishing		very high VOC	1.36
VOCs	methyl ethyl ketone	propylene glycol			

Samples selected for validation studies

Sample #		Category	Product	Type	solids (lb/gal)
61		Varnishes - Clear		high VOC	2.49
VOCs	triethyl amine	propylene glycol	dipropylene glycol monomethyl ether	N-methyl pyrrolidinone	propylene glycol monobutyl ether
	Surfynol				
55		Rust Preventative		high VOC	4.47
VOCs	2-butanol	2-butoxyethanol	butyl carbitol		
60		Metallic		unusual solvents	4.99
VOCs	propylene glycol	diethylene glycol monomethyl ether	propylene glycol monobutyl ether	2-(2-ethylhexyl) ethanol	triethylene glycol
	dibutyl phthalate				
14		High Temperature		exempt solvent(s)	3.94
VOCs	toluene	metachloro benzotrifluoride	parachloro benzotrifluoride	ethylbenzene	m,p-xylene
	o-xylene	Aromatic 100	naphthalene		
44-2		Magnesite Cement		exempt solvent(s)	2.39
VOCs	acetone	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
	naphthalene				
57-3		Lacquers		exempt solvent(s)	1.83
VOCs	methanol	acetone	2-propanol	methyl acetate	MEK
	1-butanol	butyl acetate	ethylbenzene	m,p-xylene	2-heptanone
	o-xylene	2-butoxyethanol	4-methyl-3-heptanone		

#55 Waterborne air-dry rust preventative coating

	Lab 1, Cal Poly 6890				Lab 2, BAAQMD			Lab 3, CARB		
	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
2-butanol	0.0337	0.0342	0.0333	0.0337			0.0270			Not reptd
2-butoxyethanol	0.0582	0.0578	0.0588	0.0583			0.0592			0.0596
butyl carbitol	0.0138	0.0142	0.0147	0.0142			0.0135			0.0096
Total VOC fraction	0.1057	0.1063	0.1067	0.1062			0.0997			
Density, g/L				1237	1247	1252	1250			1252
solids fraction				0.4330	0.4258	0.4263	0.4261			0.4392
water fract, calcd				0.4608			0.4743			
L water, calcd				0.5701			0.5926			
water fract, direct				0.4560	0.4734	0.4679	0.4707	0.4458	0.4210	0.4334
L water, direct				0.5641	0.5905	0.5858	0.5881	0.5581	0.5271	0.5426
Mat VOC, GC	131	131	132	131			125			
Ctg VOC, GC	304	306	307	306			306			
Mat VOC, EPA 24				137	126	132	129	144	175	160
Ctg VOC, EPA 24				315	307	320	313	326	370	349
Mat VOC, reptd										
Ctg VOC, reptd	318									

#60 Waterborne air dry metallic pigmented coating

	Lab 1, Cal Poly 6890			Lab 2, CARB			Lab 3, Cal Poly 5890		
	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
2-butoxyethanol	Not reptd	Not reptd				0.0200			
propylene glycol	0.0441	0.0447	0.0444			0.0690	0.0374	0.0377	0.0376
diethylene glycol monomethyl ether	0.0278	0.0282	0.0280			Not reptd	0.0274	0.0237	0.0255
propylene glycol monobutyl ether	0.0164	0.0167	0.0166			Not reptd	0.0121	0.0146	0.0133
2-(2-ethylhexyl)ethanol	0.0142	0.0153	0.0148			Not reptd	0.0158	0.0152	0.0155
triethylene glycol	0.0037	0.0040	0.0038			Not reptd	0.0000	0.0000	0.0000
Total VOC fraction	0.1062	0.1089	0.1075				0.0926	0.0913	0.0920
dibutyl phthalate	0.0195	0.0168	0.0181			Not reptd	0.0236	0.0219	0.0227
Density, g/L			1200			1216			1195
solids fraction	0.4995	0.4972	0.4983			0.5076	0.4975	0.4974	0.4975
water fract, calcd	0.3943	0.3940	0.3941				0.4098	0.4114	0.4106
L water, calcd	0.4734	0.4729	0.4731				0.4920	0.4938	0.4929
water fract, direct			0.3854	0.4164	0.3771	0.3967			0.3854
L water, direct			0.4627	0.5063	0.4586	0.4824			0.4606
Mat VOC, GC	127	131	129				111	109	110
Ctg VOC, GC	242	248	245				218	215	217
Mat VOC, EPA 24	138	141	140	92	140	116	140	140	140
Ctg VOC, EPA 24	257	262	260	187	259	225	259	260	259
Mat VOC, reptd									
Ctg VOC, reptd	< 250								

#76-1 Waterborne air-dry faux finish

	Lab 1, Cal Poly 6890					Lab 2, CARB			Lab 3, Cal Poly 5890		
analyte	Run 1	Run 2	Run 3	Run 4	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
UK	0.0056	0.0084	0.0055	0.0080	0.0069			Not reptd			
MEK	0.0114	0.0063	0.0044	0.0060	0.0070			Not reptd	0.0161	0.0097	0.0129
UK	0.0005	0.0009	0.0006	0.0008	0.0007			Not reptd			
UK	0.0012	0.0018	0.0013	0.0015	0.0014			Not reptd			
propylene glycol	0.3028	0.2520	0.2593	0.2890	0.2758			0.2696	0.2699	0.2856	0.2778
UK	0.0045	0.0049	0.0035	0.0045	0.0043			Not reptd			
Total VOC fraction	0.3261	0.2742	0.2745	0.3098	0.2962			0.2696	0.2923	0.2856	0.2890
Density, g/L					1074			1093			1084
solids fraction	0.1517	0.1515			0.1516			0.1560	0.1511	0.1510	0.1511
water fract, calcd	0.5222	0.5743	0.5739	0.5386	0.5522	0.5487	0.5088	0.5744	0.5566	0.5633	0.5600
L water, calcd	0.5609	0.6169	0.6164	0.5786	0.5932	0.5997	0.5561	0.6278	0.5979	0.6051	0.6015
water fract, direct					0.5747			0.5287			0.5747
L water, direct					0.6173			0.5779			0.6227
Mat VOC, GC	350	295	295	333	318			295	317	310	313
Ctg VOC, GC	798	769	769	790	782			792	788	784	786
Mat VOC, EPA 24					294	323	366	345			297
Ctg VOC, EPA 24					768	806	825	816			788
Mat VOC, reptd											
Ctg VOC, reptd	Not Reptd										

#44-2 Solventborne air-dry magnesite cement coating

	Lab 1, Cal Poly 6890			Lab 2, BAAQMD			Lab 3, CARB
	Run 1	Run 2	Average	Run 1	Run 2	Average	Average
acetone	0.4700	0.4688	0.4694	0.4111	0.4330	0.4221	0.4520
ethylbenzene	0.0138	0.0137	0.0138			0.0161	0.0179
m,p-xylene	0.0567	0.0564	0.0565			0.0607	0.0592
o-xylene	0.0217	0.0218	0.0217			0.0230	0.0259
UK	0.0124	0.0108	0.0116				
Aromatic 100	0.1378	0.1169	0.1274			0.1470	Not reptd
naphthalene	0.0115	0.0099	0.0107			0.0105	Not reptd
Total volatile fraction	0.7239	0.6983	0.7111			0.6783	
acetone. L	0.5246	0.5232	0.5239	0.4673	0.4944	0.4808	0.5126
Total VOC fraction	0.2539	0.2295	0.2417	0.2672	0.2453	0.2563	
Mass Balance, fract			1.0302			0.9863	
Density, g/L			883	899.1	903.1	901.1	897
solids fraction	0.3219	0.3262	0.3241	0.3074	0.3086	0.3080	0.3470
Matl VOC, GC	224	203	213	240	222	231	
Coat VOC, GC	472	425	448	451	438	445	
Matl VOC, EPA 24	184	181	182	253	233	243	180
Coat VOC, EPA 24	387	380	383	475	462	469	370
Matl VOC, reptd	192						
Coat VOC, reptd	419						
Acetone fraction, reptd	0.4844						

Precision data for Sample #44-2

Between-laboratory standard deviations:

material VOC, GC = 12.4 g/L

coating VOC, GC = 2.5 g/L

material VOC, EPA 24 = 35.7 g/L

VOC, EPA 24 = 53.5 g/L

acetone fraction = 2.18%

Summary results from round-robin of 2K coatings

	VOC g/L			
Sample #3, solventborne	Cal Poly 6890	Cal Poly 5890	Industrial	SCAQMD
Material VOC by GC	178	181	227	
Coating VOC by GC	178	181	227	
Material VOC by EPA 24	168	179	183	159
Coating VOC by EPA 24	168	179	183	162
Coating VOC rept. Manuf.	180			
Sample #15-2, solventborne				
Material VOC by GC	115	161	167	
Coating VOC by GC	115	161	167	
Material VOC by EPA 24	54	44	69	53
Coating VOC by EPA 24	54	44	69	54
Coating VOC rept. Manuf.	12			
Sample #15-3, solventborne				
Material VOC by GC	211	230	226	
Coating VOC by GC	211	230	226	
Material VOC by EPA 24	227	218	238	231
Coating VOC by EPA 24	227	218	238	233
Coating VOC rept. Manuf.	214			
Sample #26, waterborne				
Material VOC by GC	114	127	133	
Coating VOC by GC	193	211	222	
Material VOC by EPA 24				-51
Coating VOC by EPA 24				-134
Material VOC rept. Manuf.	122			
Coating VOC rept. Manuf.	236			
Sample #45, waterborne				
Material VOC by GC	85	89	102	
Coating VOC by GC	220	234	244	
Material VOC by EPA 24				91
Coating VOC by EPA 24				278
Material VOC rept. Manuf.	82	rept. 3rd party	68	
Coating VOC rept. Manuf.	244	rept. 3rd party	223	

15-2 solventborne 2K industrial maintenance coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
benzyl alcohol	0.1164	0.0699	0.0629	0.0830	0.1033	0.1082	0.1367	0.1161	0.0943	0.1332	0.1332	0.1202	
Total VOC fraction	0.1164	0.0699	0.0629	0.0830	0.1033	0.1082	0.1367	0.1161	0.0943	0.1332	0.1332	0.1202	
benzyl alcohol in UNCURED SAMPLE	0.1158												
Density, g/L				1385				1385				1385	1400
solids fraction	0.9619	0.9612	0.9605	0.9612	0.9693	0.9682	0.9675	0.9683	0.9516	0.9461	0.9537	0.9505	0.9560
KF water fraction													0.0060
KF water, L													0.0084
Mass balance, fraction	1.0783	1.0311	1.0233	1.0442	1.0726	1.0764	1.1042	1.0844	1.0459	1.0793	1.0869	1.0707	
Material VOC by GC	161	97	87	115	143	150	189	161	131	184	184	167	
Coating VOC by GC	161	97	87	115	143	150	189	161	131	184	184	167	
Material VOC by EPA 24	53	54	55	54	43	44	45	44	67	75	64	69	53
Coating VOC by EPA 24	53	54	55	54	43	44	45	44	67	75	64	69	54
Coating VOC reported by manufacturer	12												

#15-2 solventborne 2K industrial maintenance coating Effect of film thinkness on D-2369 determination

Sample 15-2. Recommended film thickness = 6 - 12 mils					
	volatile fraction				
	trial 1	trial 2	trial 3	average	coating VOC based on average
D2369, FT=6.5 mils	0.0349	0.0350	0.0357	0.0352	49
D2369, FT= 11.4 mils	0.0242	0.0239	0.0205	0.0229	32
GC, 6.5 mils, extract 5 sec	0.0383	0.0459		0.0421	58
GC, 6.5 mils, extract 24 hour	0.0625	0.0484		0.0554	77
benzyl alcohol, uncured mixture	0.1158	0.1164		0.1161	161
Reported Coating VOC					12

The VOC content of waterborne 2K coatings can be determined by direct GC analysis

- No EPA method for measuring VOC of waterborne 2K coatings
- 2 waterborne 2K coatings analyzed by Cal Poly (2 labs), industrial lab and SCAQMD (Method 24 only)

Sample	Solids Fraction	Water Fraction, calcd	Material VOC, GC g/L	Coating VOC, GC g/L	Std Dev, Material VOC g/L	Std Dev, Coating VOC g/L	Rept, MaterialVOC g/L	Rept, Coating VOC g/L
#26	0.57	0.33	125	209	9	15	122	236
#45	0.28	0.58	92	233	9	12	82, 68	244, 223

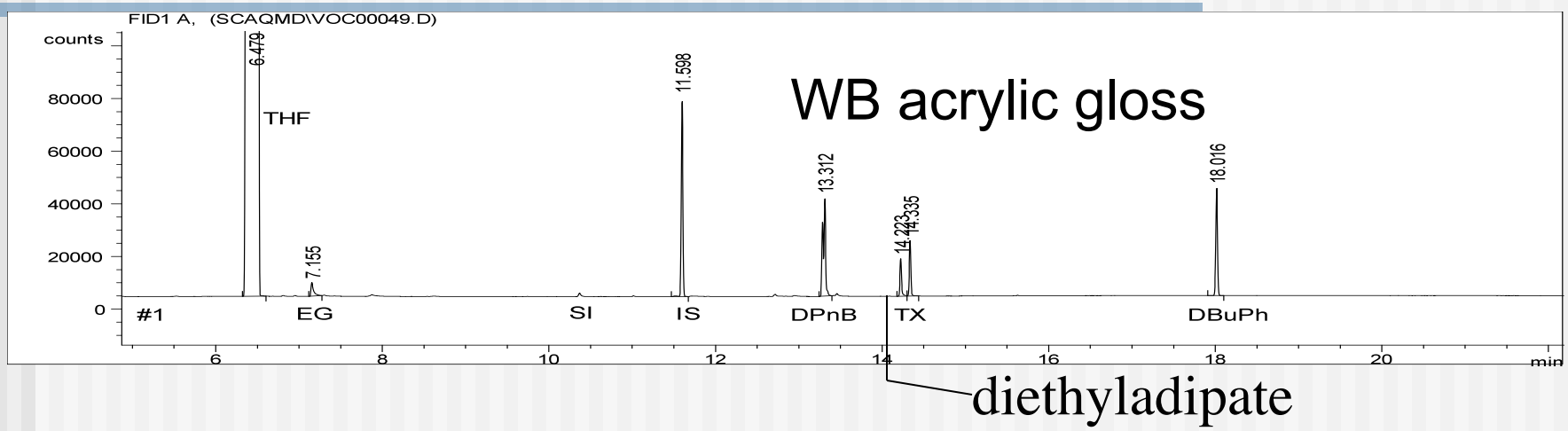
#26 Waterborne 2K swimming pool coating

	Cal Poly 6890				Cal Poly 5890				Industry				SCAQMD
	Lab 1				Lab 2				Lab 3				Lab 4
VOC	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	Run 1	Run 2	Run 3	Average	
2-propoxyethanol	0.0829	0.0804	0.0809	0.0814	0.0906	0.0851	0.0786	0.0848	0.0997	0.0986	0.0976		
Aromatic 100	0.0130	0.0116	0.0132	0.0126	0.0162	0.0159	0.0267	0.0196	0.0105	0.0105	0.0105		
Total VOC fraction	0.0959	0.0920	0.0941	0.0940	0.1068	0.1010	0.1052	0.1044	0.1102	0.1091	0.1081	0.1091	
Density, g/L				1217				1217				1217	1280
solids fraction	0.5702	0.5715	0.5721	0.5713	0.5667	0.5686	0.5689	0.5681	0.5600	0.5580	0.5630	0.5603	0.5570
calcd water fraction	0.3339	0.3365	0.3338	0.3347	0.3265	0.3304	0.3259	0.3276	0.3298	0.3329	0.3289	0.3305	
calcd water, L	0.4063	0.4094	0.4061	0.4073	0.3972	0.4020	0.3964	0.3985	0.4012	0.4050	0.4002	0.4021	
KF water fraction													0.4830
KF water, L													0.6182
Material VOC by GC	117	112	115	114	130	123	128	127	134	133	132	133	
Coating VOC by GC	196	189	193	193	216	206	212	211	224	223	219	222	
Material VOC by EPA 24													-51
Coating VOC by EPA 24													-134
Material VOC reported by manufacturer	122												
Coating VOC reported by manufacturer	236												

Summary of validation studies

- when similar procedures were followed, labs obtained results in good agreement
- some labs were unable to analyze all of the VOCs present in some samples
- problems with Method 24 water determinations were seen, as expected
- in some cases, CARB Method 310 gave results in agreement with ASTM D6886
- VOCs of solventborne 2K coatings may be measured by direct GC or EPA Method 24
- VOCs for 2K coatings with > 90% solids must be determined using a modification of EPA Method 24
- VOCs of waterborne 2K coatings cannot be measured by EPA Method 24 but can be determined using direct GC

The future? VOC defined by boiling point marker



ISO 11890-2, Paints and varnishes – Determination of volatile organic compound (VOC) content – Part 2: Gas-chromatographic method - uses a boiling point limit of 250^0C and defined chromatographically by the retention time of diethyl adipate on a 60m poly(6% cyanopropylphenyl/94% dimethylsiloxane) (DB-1301^{TM}) capillary column.

Summary

- A suite of VOC analysis methods was developed for use in analyzing any architectural coating sold in California
- For high VOC solventborne coatings with no exempt compounds, EPA Method 24 provides an accurate and simple procedure for determining VOC
- Methods similar to ASTM D6886 were tested on 67 coatings
- These new methods were tested against those used by regulatory agencies and industry and were found to be at least equal in quality and generally superior to other methods.
- A California Manual for Determination of the VOC Content of Architectural Coatings was developed.

VOC Manual

APPENDIX : California Manual for Determination of the VOC Content of Architectural Coatings

This manual is a compilation of new methods developed at California Polytechnic State University and a listing of required existing methods for use in the determination of the VOC content of all architectural coatings sold in California. These new methods are under development and have been presented to ASTM and will be submitted for comment and balloting before the end of the year. This manual is not intended to replace any of the existing district methods manuals but is intended to complement them. This manual will be revised on a regular basis to incorporate new methods and to update changes in existing methods.

Links:

- California Manual for Determination of the VOC Content of Architectural Coatings (and final report for this project)
  - http://www.arb.ca.gov/coatings/arch/testmethod.htm
- Questions, comments?
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